



Solution processed alkali-metal and alkaline-earth-metal compounds as the efficient electron injection layer in organic light-emitting diodes

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ABSTRACT

To enable the use of high work-function metals as the cathode in organic light emitting diodes (OLEDs), different types of alkali-metal and alkaline-earth-metal based compounds are examined as the electron injection layer (EIL). All the studied compounds can improve the device performance for aluminum, gold, and silver cathodes. Potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) are employed as EIL for the first time in OLEDs. The performance of the device with sodium hydroxide (NaOH)/silver cathode almost doubles the conventional barium/aluminum device's efficiency. By examining the work-function of EIL-modified metals through Kelvin Probe, a general correlation between the device performance and cathode work-function is revealed. The image-charge effect is found to be a contributor to the reduction of the metal work-function.

1. Introduction

Organic light emitting diodes (OLEDs) are solid light sources with unique features of solution-processibility, flexibility, and lightweight. Despite of their tremendous success in the application of display in recent years, further improvements on device performance are still required. Conventional high-efficiency devices employ low work-function metals, such as Ba, Ca, Mg, as cathodes to achieve low electron injection barrier [1–3]. However, the low work-function metals are extremely sensitive to moisture and oxygen, making elaborate encapsulation a prerequisite [4]. Using more environmentally stable metals as the electrode, such as Al, Au, and Ag, can simplify the encapsulation, thereby lowering the cost. However, the work-function of the environmentally stable metals is relatively high for common organic emission materials, leading to inferior device performance.

To reduce the electron injection barrier for the high work-function cathodes, electron injection layer (EIL) has to be introduced. Various materials, such as organic surfactants, self-assembled molecules, and metal oxides, have been explored [5–10]. Particularly, alkali-metal and alkaline-earth-metal based compound have been found to be efficient in improving electron injection and device stability [11–15]. Thermally evaporated LiF and CsF are commonly used due to their excellent device efficiency and air stability [16,17]. However, a theory has yet to be universally accepted to

explain the function of the compounds as EIL. Various models have been proposed, including dipole formation at the interface, *n*-doping to the organic layer, and chemical reaction with the metal [13,15,16,18].

In this work, different types of solution-processed alkali-metal and alkaline-earth-metal based compounds have been investigated as EIL in OLEDs. High work-function metals of Al, Ag, and Au are employed as the cathode. It is found that by simple solution deposition, the compounds can increase device current and show superior efficiency than the devices without EIL. Generally, the compounds which work for Al also work for Ag and Au cathodes, indicating a common working mechanism. Correlation of the EIL-modified cathode work-function and the device performance suggests that the interfacial dipole induced by image-charge effect is the main contributor to the lowered electron injection barrier. The sodium hydroxide (NaOH)/Ag device shows better performance than the conventional Ba/Al device, confirming NaOH's potential application as EIL in low-cost and high-efficiency devices.

2. Experimental section

2.1. Materials

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was purchased from 1-Material Inc., and dissolved in

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Table 1
Solvents for the EIL materials and optimized concentrations for the best device efficiencies.

EIL	Solvent	Concentration (wt%)	Water contact angle ^a (°)
LiOH	methanol	0.1	98.4
NaOH	ethanol	0.1	99.3
KOH	ethanol	0.1	92
Ba(OH) ₂	ethanol	0.1	75
Na ₂ CO ₃	H ₂ O:EtOH (1:3 v/v)	0.2	100.6
K ₂ CO ₃	H ₂ O:EtOH (1:3 v/v)	0.1	97.6
Cs ₂ CO ₃	ethanol	0.1	95
Bare MEH-PPV	–	–	102.7

^a The water contact angles are measured on the EIL modified MEH-PPV layer.

chlorobenzene at 0.5 wt%. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOS™ P VP Al 4083) was purchased from Heraeus Holding GmbH. The alkali-metal and alkaline-earth-metal based compounds were purchased from Sigma-Aldrich. They were dissolved and filtered before spin-coating.

2.2. Device fabrication and characterization

Indium tin oxide (ITO)-coated glass (China Southern Glass Holding Corp.) was used as the substrate (sheet resistance of 15–20 Ω per square). Prior to device fabrication, the substrates were thoroughly cleaned in ultrasonic bath of acetone, isopropanol, detergent, de-ionized water, and isopropanol in sequence, followed by being dried in a baking oven for over 2 h. The ITO was treated with oxygen plasma for 20 min before the PEDOT:PSS layer (40 nm) was spin-coated on top. Subsequently, the substrate was baked at 180 °C in nitrogen for 10 min. After a 80 nm thick MEH-PPV layer was spin-coated on top of the PEDOT:PSS layer from a 0.5 wt% chlorobenzene solution, the alkali-metal and alkaline-earth-metal based compounds, or the pure ethanol, was spin-coated on top of the MEH-PPV at 2000 rpm. Finally, 120 nm aluminum was thermally evaporated with a shadow mask to form the top electrode under the pressure of 10^{−4} Pa. The device emission area is 15 ± 0.1 mm². The thin film thickness was measured by a Dektak 150 surface profiler. The current-voltage-luminance characteristics were measured by a Keithley 236 source meter and a silicon photodiode calibrated by a Konica Minolta Chroma Meter CS-200.

3. Results and discussion

For depositing the solution-processed EIL on top of organic layers, orthogonal solvents are preferred in order to avoid corrosion of the underlying materials. Ethanol, methanol, and ethanol with a small amount of water added, are selected to dissolve the alkali-metal and alkaline-earth-metal compounds. Compounds based on various cations (Li, Na, K, Ba) and anions (−OH and −CO₃) have been tested. Lithium hydroxide (LiOH), NaOH, potassium hydroxide (KOH), barium hydroxide (Ba(OH)₂), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and cesium carbonate (Cs₂CO₃) are chosen due to their good solubility (at about 1 wt%) as listed in Table 1. Among them, KOH and K₂CO₃ are employed as EIL for the first time in OLEDs. The materials are spin-coated on top of the emission layer, MEH-PPV. The water

contact angle decreases after EIL deposition, confirming the existence of the EIL on the organic layer. To study the EILs, OLED devices with the device configuration of ITO/PEDOT:PSS (spin-coated)/MEH-PPV (spin-coated)/EIL (spin-coated)/metal (thermal-evaporated) are fabricated. The metals are Al, Ag, and Au, respectively. Since the EIL compounds are intrinsically insulating, the contact resistance could increase if the layer were too thick. To optimize the thickness, different concentrations have been tested. The best device performance is achieved when the concentration is around 0.1–0.2 wt%, as shown in Table 1.

Fig. 1 shows the current-density, luminance, and current efficiency characteristics of the devices incorporating different EILs. The cathode metal is Al, Ag, or Au. Since the bulk of MEH-PPV layer is not affected by different EIL materials, the electroluminescence spectra of the devices share the same profile as shown in Fig. 2a. Device performances are summarized in Table 2. The external quantum efficiency (EQE) is calculated from the emission spectrum under the assumption that the device is an ideal Lambertian emitter. The device with Ba/Al cathode is fabricated as the reference. Devices in which the organic/metal interface is treated with pure ethanol are fabricated to take into account the alcoholic-solvent-effect [8,19]. Because MEH-PPV is a p-type semiconductor, and PEDOT:PSS layer is an efficient hole injection layer, the hole current dominates the device current. As a result, the current densities of all the devices with different EILs are at the same level. Moreover, the device's opto-electronic properties will be determined by the injection of the minority charge, i.e. electron. For devices with Al cathodes, Ba/Al device shows a low turn-on voltage V_{on} (defined as the voltage at ~1 cd/m²) at 2.20 V, a maximum luminance (L_{max}) of 1.19 × 10⁴ cd/m², and a maximum current efficiency (CE_{max}) of 2.04 cd/A. Without Ba, the EtOH/Al device's V_{on} increases to 2.75 V, and L_{max} is only 169 cd/m². However, after inserting the EILs, device performance improves significantly. V_{on} is reduced drastically to ca. 2.00 V, smaller than that of the Ba/Al device. The best efficiency is obtained by NaOH/Al, reaching 2.90 cd/A.

For Ag cathode devices, electron injection becomes more difficult, because Ag (4.54 eV) has a larger work-function than Al (3.36 eV). Device's turn-on voltage is 4.25 V, much larger than that of Al cathode devices. After EILs are incorporated, the V_{on} is substantially reduced to 3.00 V (LiOH/Ag), 2.75 V (NaOH/Ag), 2.50 V (KOH/Ag), and 2.25 V (K₂CO₃/Ag), respectively. L_{max} of NaOH/Ag reaches 1.29 × 10⁴ cd/m², which are more than 20 times higher than that of EtOH/Al device. Device efficiency of NaOH/Ag is 3.76 cd/A, which is better than the best Al cathode device of NaOH/Al (2.90 cd/A), and almost doubling the reference Ba/Al device (2.04 cd/A).

For Au cathode devices, without EIL, the EtOH/Au device cannot emit light, indicating negligible electron injection due to the high work-function of Au (4.98 eV). After incorporating the EILs, all devices emit light. The best device performance is achieved by KOH/Au. The turn-on voltage is 2.25 V, L_{max} reaches 2.21 × 10³ cd/m², which is better than that of the EtOH/Al device.

To investigate the electron injection barrier, the work-functions of the EIL modified metal cathodes are characterized by Kelvin Probe in the nitrogen-filled glovebox (Table 1) [20,21]. It is observed that all EILs can form a dipole layer and lower the metal work-function. The largest reductions are obtained on Al/NaOH (2.67 eV), Ag/NaOH (3.86 eV), and Au/LiOH (3.79 eV). Previous studies suggest that the surface work-function change introduced by ionic species is caused by image-charge effect at the interface [22,23]. Generally, substrates with higher dielectric-constant ϵ form stronger image charges, thereby inducing a larger dipole in the EIL. Fig. 2 shows the work-function change of the EILs on various substrates, including high- ϵ substrates (Al, Ag,

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